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ARTICLE

Oligothienyl catenated germanes and silanes: synthesis, structure, properties

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The synthesis of two new groups of oligothienyl catenated silanes and germanes, $\text{Me}_5\text{M}_2\text{Th}_n$ (**1a-b**), $\text{Me}_5\text{M}_2\text{Th}_n\text{M}_2\text{Me}_5$ (**2a-c**) (terminal), and $\text{Th}_n\text{M}_2\text{Me}_4\text{Th}_n$ (**3a-d**) (internal) ($\text{M} = \text{Si}, \text{Ge}$; $n = 2, 3$; $\text{Th} = 2\text{- or } 2,5\text{-thienyl}$) is reported. The study of their structural parameters as well as of their spectral (NMR), electrochemical (CV) and optical (UV/vis absorbance, luminescence) properties has been performed in detail; in addition, the unexpected compound $[\text{Th}_2\text{Si}_2\text{Me}_4\text{Th}]_2$ (**3a'**) is also studied. Theoretical investigations have been performed for model compounds in order to establish structure – property relationships. The molecular structures of **2a** ($\text{Me}_5\text{Si}_2\text{Th}_2\text{Si}_2\text{Me}_5$), **2b** ($\text{Me}_5\text{Ge}_2\text{Th}_2\text{Ge}_2\text{Me}_5$), **3a** ($\text{Th}_2\text{Si}_2\text{Me}_4\text{Th}_2$) and **3b** ($\text{Th}_2\text{Ge}_2\text{Me}_4\text{Th}_2$) have been investigated by X-ray diffraction analysis. An effective conjugation with flattening of both Th planes in terminal **2a** and **2b** was observed. The main trends in the dependence of the optical and electrochemical properties on the structural parameters have been established. All of the compounds studied exhibit a strong emission within the 378–563 nm range, the maximal quantum yield (up to 77 %) is observed for the Si derivative **3a'**. For the majority of the compounds the quantum yields (20–30 %) are significantly larger than for 2,2'-bi- and 2,2':5',5'-terthiophenes. Due to their good emission properties, these compounds could be used to develop new materials with specific spectral properties.

Introduction

Nowadays investigations of molecular catenated derivatives based on Group 14 elements represent a significant scientific challenge in order to understand their specific physicochemical properties.¹ The unique properties of these catenated compounds (strong UV/vis absorbance, luminescence, conductivity as well as non-linear optical properties) which are appeared due to an effective σ -conjugation through the M–M bonds ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$),² open endless possibilities for the practical application of such compounds; several Si derivatives are already used as new materials (as field-effect transistors (FET),³ semiconductors,^{4–5} etc.).

Most of the works published in the field concerns the study of oligosilyl derivatives.⁶ As shown by Kira,⁷ Kyushin,⁸ Nishihara,⁹ Marschner¹⁰ *et al.* and others,¹¹ the properties of these compounds strongly dependent on the nature of their organic substituents (σ - π -conjugation) and on the geometry of the molecule. Among the Group 14 elements, tin compounds have attracted the least interest presumably due to their possible toxicity and weak Sn–Sn bond.¹² Furthermore, little attention has been paid to the Ge analogs.¹³ A significant interest has been given to polymeric compounds (especially, polysilanes¹⁴ and their application as semiconductors and photoresistors,¹⁵ in nonlinear optical¹⁶ and in luminescence¹⁷). Only few polygermanes have been reported up to date.¹⁸

The previous investigations of the chemical, structural, and physical properties of molecular oligogermanes performed by Marschner,¹⁹ Weinert *et al.*²⁰ and our group²¹ have shown the strong dependence between the physical properties of these compounds and their conformation, the nature of the substituents at M, the nature and the number of the M atoms.

Organic π -conjugated linear oligomers with well-defined structures such as oligothienyl derivatives are attracting significant attention as new materials with useful physical properties²² (conductive charge-transfer complexes and chemically doped materials based on such derivatives have recently been reported^{23–24}). Furthermore, thienyl substituents are usually regarded as electron donating groups, and

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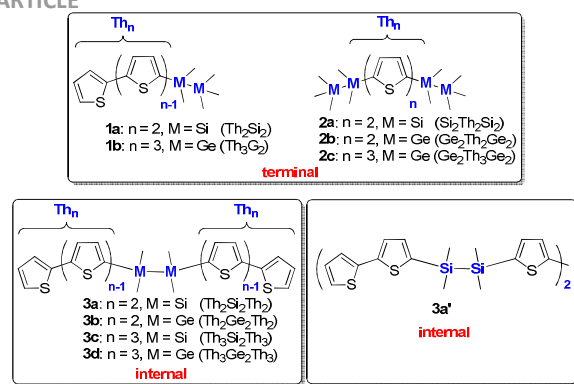
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Electronic Supplementary Information (ESI) available: Synthetic procedures for the initial Ge compounds and Th_2 , Th_3 ; table of crystallographic data (Table S1) for compounds **2a**, **2b**, **3a** and **3b**; NMR spectra of the compounds synthesized in this work (Figs. S1–S38); UV/vis and luminescence spectra (Figs. S39–S48); DFT data (Tables S2–S6, Figs. S49–S56) and computational details; electrochemistry CV curves (Figs. S57–S68) (PDF); crystallographic data for compounds **2a**, **2b**, **3a** and **3b** (CIF); calculated structures (XYZ). See DOI: 10.1039/x0xx00000x.

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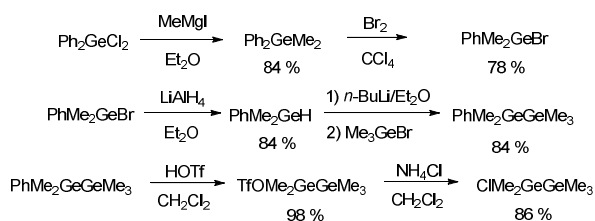


frequently used as electron pools in donor-acceptor type carbon π -type materials.^{22b} Up to now, only few conjugated molecular²⁵ and polymeric²⁶ compounds containing oligothieryl and one- or several Si atoms have been reported and the relationships between their structure and physical properties have not been fully explored. Therefore, the study of the smallest structural and electronic building blocks responsible for the appearance of the useful physical properties represents a crucial task for the future development of new functionalized material based on Group 14 compounds. The oligomeric compounds may be regarded as model for polymers and simulate their properties due to a well-defined structure and a high solubility. The range of molecular heterocyclic oligosilanes is limited and so far, no Ge derivatives of such compounds have ever been reported before. No comparative investigation of the series of related compounds has ever been performed also. Such “structure – property” relationships are very useful for the elaboration of new materials with interesting characteristics. Combining in one molecule several functional groups, M_n and Th_n , where each of them possesses unique properties, would results in new properties and relationships. This also represents an actual synthetic challenge.

The main target of this work is to produce a systematic research where series of oligothieryl substituted catenated Group 14 derivatives are synthesized and their properties studied in detail. Two main groups (terminal and internal) of thienyl substituted catenated Group 14 derivatives were studied (Chart 1), they differ in the substitution of the thienyl framework (mono- or disubstituted terminal or internal derivatives), the nature of the element ($M = Si, Ge$) and in the number of thienyl rings (two or three). Bi- and terthienyl groups may be considered as the simplest models, and the corresponding starting materials (Th_2 and Th_3) for their insertion are readily available.

Detailed procedures for the synthesis of **1a-b**, **2a-c**, **3a-d**, and the unusual product $[Th_2Si_2Th_2]_2$ (**3a'**), investigation of their structure in solution (by multinuclear NMR) and in solid state (by single crystal X-ray diffraction analysis), studies of their optical (UV/vis, luminescence spectroscopy) and electrochemical properties (by cyclic voltammetry) as well as theoretical investigation (by DFT) are presented in this work.

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The correlation between their physical properties and the nature of the M atom, the number of M and Th and the type of substitution (internal or terminal), are established.

Results

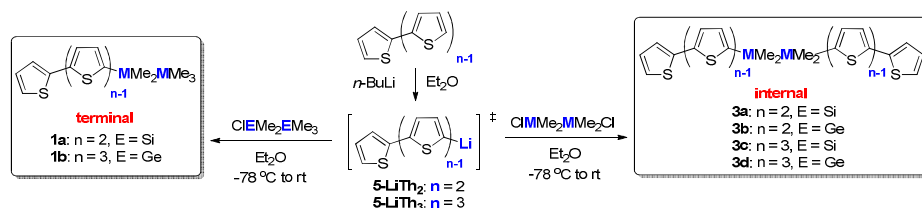
Synthesis

The synthesis of chloropentamethyldigermane as one of the initial germanium compounds was performed as described in Scheme 1 (for details, see ESI, Figs. S1–S13).

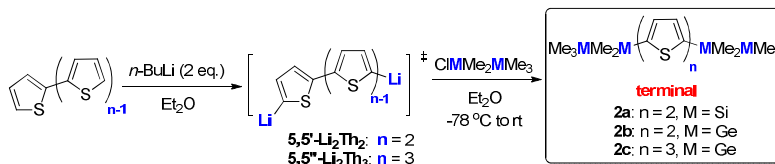
This 6 steps synthesis affords $ClGeMe_2GeMe_3$ with a yield of 39 %; such synthetic strategy may be useful for the synthesis of related derivatives. During the first stage, the methylation of Ph_2GeCl_2 by a Grignard reagent results in the formation of Ph_2GeMe_2 . This way of synthesis applying phenyl derivative is more convenient than any alternatives relying on the use of Me_2GeCl_2 due to availability of initial compound in laboratory.²⁷ The second step consists in an electrophilic bromodephenylation by molecular bromine resulting in the formation of $PhMe_2GeBr$. After reduction by $LiAlH_4$, $PhMe_2GeH$ is germylated by reaction with Me_3GeBr due to the acidic nature of the Ge–H bond. This procedure is more selective than the ones that relies on the use of amalgamated Mg.²⁸ A mild selective removal of Ph groups from the oligogermanes by the action of $HOTf$ ^{21a,29} followed by a subsequent nucleophilic substitution by NH_4Cl resulted in the formation of the desired compound $ClGeMe_2GeMe_3$. This procedure leads to the formation of the pure target compound without the need for any further purification or separation of $ClGeMe_2GeMe_3$ from by-products (such as $ClGeMe_2GeMe_2Cl$ ³⁰). A similar synthetic way was reported earlier by Nuckolls *et al.*^{5b} without the isolation of the intermediate compounds. The detailed procedures for the synthesis of Th_2 and Th_3 are also given in the Supporting Information.

The synthesis of the target thienyl compounds was performed in two steps. The key reaction, a simple metalation of bi- or terthiophene by $n-BuLi$, is possible because of the higher acidity of the α -proton in these heterocyclic compounds. First, the bi- or terthiophene were lithiated giving *in situ* the corresponding mono-, 5-LiTh₂, 5-LiTh₃, or dilithiated, 5,5'-Li₂Th₂ or 5,5''-Li₂Th₃, derivatives. Then, these lithiated intermediates were treated with an electrophilic reagent, either $ClMMe_2MMe_2Cl$ or $ClMMe_3MMe_3$ ($M = Si, Ge$) giving the target compounds **1a-b**, **3a-d** and **2a-c** (Schemes 2, 3).

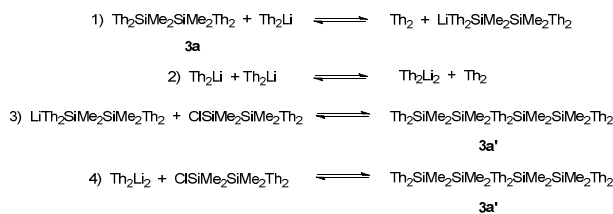
The direct lithiation of thienyl derivatives, used in this work, is a major improvement compared to the transmetalation procedure^{25d} used earlier for the generation of similar lithium thienyls. Due to its low nucleophilicity, the



Scheme 2. Synthesis of monosubstituted oligothiophenyl compounds.



Scheme 3. Synthesis of disubstituted oligothiophenyl compounds.

Scheme 4. Mechanism of formation of compound **3a'** during the synthesis of **3a**.

lithiated terthienyl derivatives, 5-LiTh₃ and 5,5''-Li₂Th₃, react slowly with Ge and especially Si chlorides. Therefore, a prolonged reaction time and a higher temperature (up to 50 h, 35 °C) were required in order to obtain the desired compound. Surprisingly, the synthesis of **3a** was successfully conducted in Et₂O while in THF a complex mixture of inseparable compounds was obtained.

During the synthesis of **3a** the unexpected compound **3a'**, [Th₂Si₂Th]₂ (Chart 1), was isolated from the reaction mixture as a minor product. A possible pathway for the formation of compound **3a'**, including the intermolecular transmetallations, is depicted in Scheme 4. According to DFT calculations, all of these reactions are reversible and have a very low energy barrier. For example, in the second reaction the equilibrium is shifted to the right by only +2 kcal/mol.

In the case of the monosubstituted derivatives, **1a** and **1b** (Schemes 2, 3), the admixtures of symmetric diadducts, **2a** and **2c**, respectively, are observed (according to NMR of the crude reaction mixtures) despite the careful control the reaction conditions (precise stoichiometry and low temperature); this could be an indirect evidence for side reactions during the monolithiation, similar to those shown on Scheme 4.

The compounds studied are slightly yellow (**2a**, **3a**, **3a'**, **3b**, **3c**, **3d**) or colorless (**1b**, **2b**, **2c**) powders or yellow colored oils (**1a**). All of the compounds are stable under inert atmosphere for a long time. However, upon exposure to air or when in solution, a slow oxidation is observed as well as the apparition of a blue and green color. All compounds have shown to be

partially soluble in toluene and totally insoluble in *n*-hexane; they are all fairly soluble in common polar organic solvents (Et₂O, CH₂Cl₂, CHCl₃, THF); the solubility of **3a'** however is lower. All of the compounds synthesized are new; only **1a**^{26a} and **2a**^{26d} have been described earlier but not fully characterized. The identity of all compounds was confirmed by elemental analysis; their structure was also confirmed by mass-spectrometry and in solution by multinuclear NMR spectroscopy (for details, see the Experimental part and ESI, Figs. S14-S38).

Structure in solid state

The molecular structures of **2a**, **2b**, **3a** and **3b** were studied by single crystal X-ray diffraction analysis (Figs. 1-4; Table S1, ESI). The geometry of Si and Ge atoms in these compounds may be described as slightly distorted tetrahedral. Crystals of these compounds were obtained by a slow evaporation of their solutions in CH₂Cl₂/*n*-octane mixture. Before this work, there were no reported structures of catenated oligothiophenyl germanes and only 7 structures (Chart 2; **A**,³¹ **B**,^{26c} **C**,^{25b} **D-F**,^{9b} **G**^{9d}) were known for the related silyl derivatives.

Molecular structures of terminal derivatives **2a** and **2b** (Scheme 3, Figs. 1, 2) are very similar. Both molecules are centrosymmetric. In **2a** the positions of the terminal SiMe₃ group are partially disordered. The planes of two thienyl groups in each case are coplanar and are in *transoid* conformation (torsion S-C-C-S is 180°). This is related to other species (like **D**, Chart 2), containing terminal M₂ blocks in polythiophenes. Furthermore, M₂Me₅ fragments are also found in *trans* position in relation to the plane of Th₂ framework and almost perpendicular to it (torsion angles C_{Th}-C_{Th}-Si-Si are 92.95(17)° for **2a** and 94.9(3)° for **2b**) indicating a high degree of conjugation for oligothiophenes with terminal catenated Group 14 substituents. This effect is more significant for Si than for Ge.

The structures of the internal derivatives **3a** and **3b** may be regarded together (Scheme 2, Figs. 3, 4). Both molecules are centrosymmetric. On contrary to **2a**, **2b**, the two thienyl

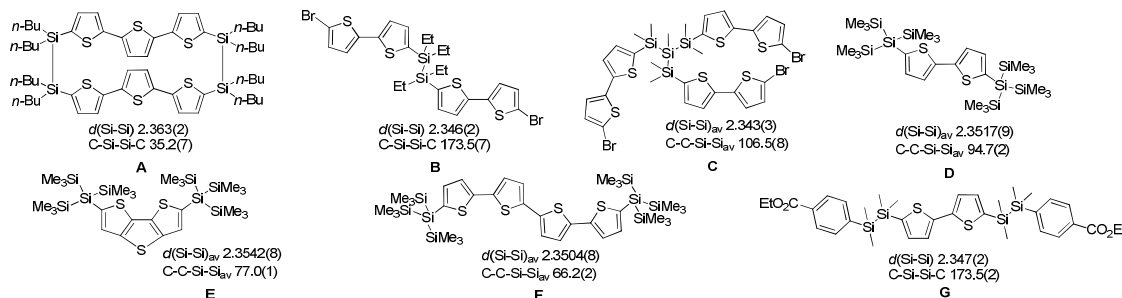
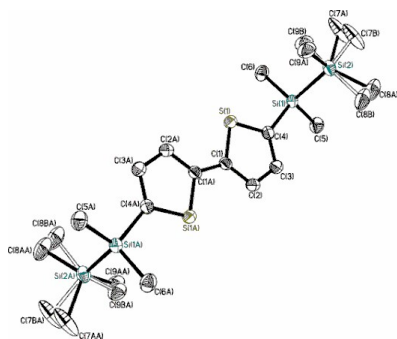
Chart 2. Compounds containing Th_2Si_2 framework investigated by XRD.

Figure 1. Molecular structure of compound $\text{Me}_3\text{SiSiMe}_2[\text{Th}]_2\text{SiMe}_2\text{SiMe}_3$ (**2a**). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Minor components of disordered groups are shown by open lines. Selected bond lengths (Å) and bond angles (deg): $\text{Si}(1)-\text{Si}(2)$ 2.3388(5), $\text{Si}(1)-\text{C}(4)$ 1.8723(13), $\text{C}(1)-\text{C}(1\text{A})$ 1.455(2), $\text{Si}(1)-\text{C}(5)$ 1.8724(14), $\text{Si}(1)-\text{C}(6)$ 1.8726(14), $\text{Si}(2)-\text{C}_{\text{av}}$ 1.876(4), $\text{C}(4)-\text{Si}(1)-\text{Si}(2)$ 108.54(4), $\text{C}(5)-\text{Si}(1)-\text{C}(6)$ 111.71(7), $\text{C}-\text{Si}-\text{C}_{\text{av}}$ 109.0(3).

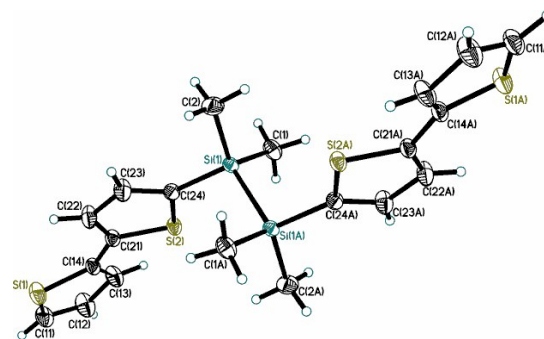


Figure 3. Molecular structure of compound $\text{Th}_2\text{SiMe}_2\text{SiMe}_2\text{Th}_2$ (**3a**). Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and bond angles (deg): $\text{Si}(1)-\text{Si}(1)$ 2.3409(7), $\text{Si}(1)-\text{C}(2)$ 1.8673(14), $\text{Si}(1)-\text{C}(24)$ 1.8730(13), $\text{Si}(1)-\text{C}(1)$ 1.8741(15), $\text{C}(14)-\text{C}(21)$ 1.4564(18); $\text{C}(24)-\text{Si}(1)-\text{Si}(1)$ 108.75(5), $\text{C}(2)-\text{Si}(1)-\text{C}(1)$ 112.61(7), $\text{C}(2)-\text{Si}(1)-\text{C}(24)$ 107.91(7), $\text{C}(24)-\text{Si}(1)-\text{C}(1)$ 108.04(6).

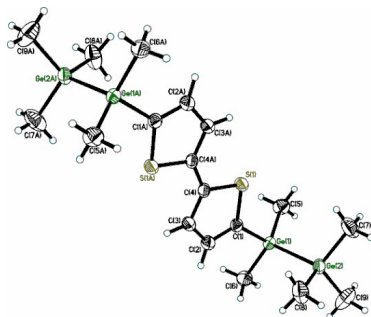


Figure 2. Molecular structure of compound $\text{Me}_3\text{GeGeMe}_2[\text{Th}]_2\text{GeMe}_2\text{GeMe}_3$ (**2b**). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): $\text{Ge}(1)-\text{Ge}(2)$ 2.4141(5), $\text{Ge}(1)-\text{C}(1)$ 1.950(2), $\text{Ge}(1)-\text{C}(5)$ 1.949(3), $\text{Ge}(1)-\text{C}(6)$ 1.957(3), $\text{Ge}(2)-\text{C}_{\text{av}}$ 1.944(3), $\text{C}(4)-\text{C}(4\text{A})$ 1.452(5), $\text{C}(1)-\text{Ge}(1)-\text{Ge}(2)$ 105.24(7), $\text{C}(5)-\text{Ge}(1)-\text{C}(6)$ 111.09(13), $\text{C}-\text{Ge}(2)-\text{C}_{\text{av}}$ 109.39(17).

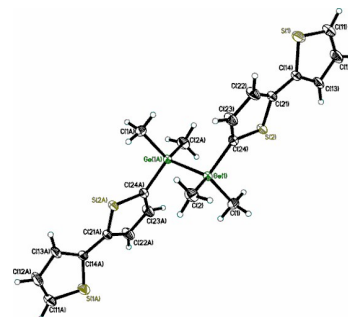


Figure 4. Molecular structure of compound $\text{Th}_2\text{GeMe}_2\text{GeMe}_2\text{Th}_2$ (**3b**). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): $\text{Ge}(1)-\text{Ge}(1\text{A})$ 2.4075(3), $\text{Ge}(1)-\text{C}(24)$ 1.9484(14), $\text{Ge}(1)-\text{C}(2)$ 1.9448(16), $\text{Ge}(1)-\text{C}(1)$ 1.9505(16), $\text{C}(14)-\text{C}(21)$ 1.454(2); $\text{C}(24)-\text{Ge}(1)-\text{Ge}(1)$ 108.27(4), $\text{C}(2)-\text{Ge}(1)-\text{C}(1)$ 112.64(8), $\text{C}(2)-\text{Ge}(1)-\text{C}(24)$ 107.39(7), $\text{C}(24)-\text{Ge}(1)-\text{C}(1)$ 107.69(6).

rings in each part of the molecule in **3a** and **3b** are not coplanar (the torsion angle between the Th rings, $\text{S}-\text{C}-\text{C}-\text{S}$, is $160.60(8)^\circ$ for **3a** and $159.06(9)^\circ$ for **3b**); they adopt a *transoid*-conformation in relation to the Th-Th carbon bond. This distortion is not perfect for a π - π -conjugation, but it is still present in both molecules. One of the most interesting features for **3a**, **3b** consists in the ideal *transoid* conformation of two Th fragments along the M_2Me_4 chain (torsion $\text{C}_{\text{Th}}-\text{M}-\text{M}-$

C_{Th} is 180°). At the same time, the torsion angle $\text{M}-\text{M}-\text{C}-\text{C}_{\text{Th}}$ ($92.02(14)^\circ$ for **3a** and $89.15(15)^\circ$ for **3b**) indicates an approximately ideal full σ - π -conjugation between M_2 and the nearest Th fragments. In other words, catenated Group 14 derivatives containing unsubstituted oligothiophenes show conjugation along the M_2 and only one Th ring. When compared to structure **B** (Chart 2), those observations could be explained by the steric volume of the alkyl substituents on the

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M atom (Me vs. Et); therefore the introduction of less sterically demanding groups into an internal position of the molecule would result in a more effective conjugation.

The analysis of the structural data suggests that the presence of substituents in 2 and 5 positions of every Th ring results in a flattening of the thienyl rings, possibly, due to packing effects. In other words, to increase of the conjugation between the M₂ and the Th_n fragments it is necessary to introduce the M fragment as an end group; small substituents on the M atom should be present as internal substitution.

UV/vis spectroscopy

The UV/visible absorption spectra for the compounds studied are given below (Table 1; Figs. S39-S44, ESI). All compounds studied show a main absorption band in the 316-372 nm range with a high molar absorptivity coefficient (higher than 10⁴), which increases with the increase of the amount of the Th groups.

In the case of polycyclic aryl substituents (in this work, oligothieryl groups) in digermanes, the main absorption is significantly bathochromic shifted in comparison to simple Ar derivatives (such as Ar₃Ge-GeAr₃, λ_{abs} 238-240 nm).^{21e} In the free Th₂ and Th₃ two bands are observed in UV/vis spectra. After introduction of a Si₂ or Ge₂ fragments, the first band (local excitation band, 244 and 250 nm, respectively, which may be regarded as a π-π* transition within the Th_n framework)³² remains approximately unchanged but its absorptivity is decreased. Furthermore, the second band (charge transfer band, excitation at 250 and 355 nm) is also bathochromically shifted except for **3d**. The red shift is more significant in the case of Si than in the case of Ge derivatives.

Luminescence

Fluorescence spectra of **1a**, **1b**, **2a-c**, **3a-d**, **3a'** in solid state (as amorphous powder) and in solution (in CH₂Cl₂) at room temperature are presented in Table 1 (Figs. S45-S48, ESI). The fluorescence occurred between 394-563 nm (in solid) and between 378-455 nm (in CH₂Cl₂), average values of Stokes' shifts (59-83 nm) are lower than for Me₃MMMe₃ derivatives.

For Group 14 derivatives the fluorescence from the locally excited state (LE)^{8a, 9c} within the phenyl ring and the intramolecular charge-transfer (ICT) emission are observed. Emission spectra shows bands with an ICT nature in solution for compounds **1a**, **2a**, **3a**, **3a'** and several types (ICT and LE) for **1b**, **2c**, **3c** (two bands in emission). For the majority of Si derivatives only one excitation and one emission process is observed; on the contrary, for the Ge compounds several emissions are observed due to several possible excitations and several pathways of emission. These differences are explained by the lower orbital energy levels in the case of Ge. As was established earlier in related derivatives,^{21c, 21e, 21f} for all compounds, studied here in solid state, the emission band is bathochromically shifted compared to the solution state (394-563 vs. 380-455 nm), and the maximal band is observed at 563 nm. In solid state, for the majority of the compounds (Table 1), the vibrational structure within the fluorescence spectra suggests the existence of a

Table 1. UV/vis absorption and luminescence emission data for compounds studied.

Compound ^a	Absorption		Luminescence			
	λ _{abs} , nm	ε*10 ⁴ , M ⁻¹ *cm ⁻¹	solid state	solution		
			λ _{em} , nm ^b	λ _{em} (nm)	Stokes shift, nm	Φ (%) ^c
Th ₂	244	2.10	389, 418,	365	64	3
	301	2.80	467, 491 (310)	(310)		
Th ₃	250	1.70	487, 511,	413	58	8
	355	2.60	537 (465)	(350)		
Me ₃ SiSiMe ₃ ^d	202	0.34	- ^f	334	132	5
				(240)	146	
				348		
				(240)		
Me ₃ GeGeMe ₃ ^e	202	-	- ^f	287	83	2
				(220)		
Th ₂ Si ₂ (1a)	240	0.46	- ^f	380	64	9
	316	1.60		(300)		
Th ₃ Ge ₂ (1b)	246	0.87	465 (290)	432	66	13
	366	2.10		(350)		
Si ₂ Th ₂ Si ₂ (2a)	246	0.39	403 (280)	394	62	49
	332	2.10	429 (280)	(320)		
Ge ₂ Th ₂ Ge ₂ (2b)	235	1.60	394 (285)	391	66	10
	325	3.90		(310)		
Ge ₂ Th ₃ Ge ₂ (2c)	240	1.40	467 (300)	431	59	15
	372	3.70		(360)	83	
				455		
				(360)		
Th ₂ Si ₂ Th ₂ (3a)	248	0.76	406 (275)	382	61	26
	321	2.00		(340)		
[Th ₂ Si ₂ Th] ₂ (3a')	233	2.40	413 (280)	393	66	76
	327	5.70		(300)		
Th ₂ Ge ₂ Th ₂ (3b)	235	0.84	397 (275)	378	59	10
	319	1.80		(310)		
Th ₃ Si ₂ Th ₃ (3c)	250	2.00	481 (290)	425	59	17
	366	5.40	533 (290)	(400)	79	
			563 (290)	445		
				(400)		
Th ₃ Ge ₂ Th ₃ (3d)	246	1.80	485 (275)	379	60	19
	319	4.70	533 (275)	(340)		

^a spectra were recorded in CH₂Cl₂
^b excitation wavelength, λ_{ex}, in parentheses; excitation wavelength was determined by excitation spectrum
^c quantum yield
^d absorption from ³³
^e absorption from ²⁸
^f oil

planar (*syn*- or *anti*-)^{26a} and a rigid quinodal form in the lower singlet excited state. Furthermore, quantum yields for our new germanium compounds (10-19 %) studied in this work were higher than for the known related digermanes (usually, less than 12 %);²¹ this might be due to a higher organizational order within the oligothieryl derivatives. The low quantum yield (9-10 %) in solution may be explained by the non-radiative quenching induced (rotation and vibrations) by the flexibility within the C and M skeleton.

Electrochemical studies

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Electrochemical investigations by cyclic voltammetry (CV) were performed for several compounds, bearing terminal M_2Me_5 (**2a**, **2b**) or internal M_2Me_4 (**3a**, **3a'**, **3b**, **3c** and **3d**) substitution (Chart 1), chosen as typical examples (Table 2; ESI, Figs. S57–S68). In terms of electrochemistry, all of the compounds have demonstrated a highly complex redox behavior. Furthermore, adsorption phenomena is observed when the electrochemical experiments were performed in CH_2Cl_2 containing $[NBu_4][PF_6]$ or $[NBu_4][BF_4]$ as supporting electrolyte. However, switching to a weakly coordinating system, DCM/ $[NBu_4][B(C_6F_5)_4]$, simplified the CV experiments by avoiding unnecessary complications arising from possible nucleophilic attacks of the electrolyte's anion on the intermediate radical-cation and by improving its solubility leading to no fouling of the electrode.³⁴ It should be noted that none of our new molecules led to a radical electropolymerization. This was confirmed by the fact that CV curves to be identical after several cycles and that no decrease of the current was observed; this is in contrast with the behaviour reported for thienyl derivatives.^{22a, 35, 36} This lack of polymerization might be explained by the presence of the catenated Group 14 fragments conjugated with the Th_n , which stabilizes the anodically generated radicals-cations. Really, it has been previously reported that α -Si thienyl groups are able to stabilize radical-cations.³⁷

In the case of terminal derivatives **2a**, **2b** (Chart 1) a second oxidation of Th_2 is observed and the oxidation of M_2 is observed as a third process. In contrary, for the internal derivatives **3a**, **3b**, **3a'** (Chart 1) after first oxidation of Th_2 , the M_2 fragment is oxidized, which leads to the rapid decomposition of the compound. In the case of terthienyl derivatives **3c**, **3d**, two irreversible oxidations of Th_3 and a subsequent oxidation of M_2 are observed. The irreversibility of this last oxidation indicates the instability of the anodically generated M-M radical-cations, what is effected by instability of M-M or M-C bond.

The values of the oxidation potentials may be used in order to estimate the HOMO (oxidation) and LUMO (reduction) energy levels,³⁸ giving HOMO-LUMO gaps between 1.5–3.0 eV, what are in good correlation with DFT calculations (see below).

Experimental data shows the dependence between the electrochemical behavior of the compounds and their structural features (terminal or internal type of substitution in oligothieryl framework, number of thienyl rings in the chain, number of catenated M atoms, nature of M). Nevertheless, as mentioned earlier, we could not completely rule out a more complex redox behavior that would encompass an anodic oxidation followed up by chemical reactions, for example rearrangements or interaction with the solvent.^{21c, 39} Several re-reduction processes have been observed and will require further investigations in order to be identified.

Discussion

Analysis of the known and obtained data

The establishment of structure – property relationships and studying a conjugation in the series of compounds proposes

Table 2. Electrochemical data for compounds according to CV.

compound	potential, V ^a	process	E _{EC} (HOMO), eV ^b	E _{EC} (LUMO), eV ^c	Gap (HOMO – LUMO), nm
2a	0.73,	3	-5.53		
	0.85, 1.21	irreversible oxidations			
2b	0.80,	3	-5.60		
	0.95, 1.29	irreversible oxidations			
3a	0.73, 1.14	2	-5.53		
		irreversible oxidations			
	-2.20	1		-2.60	423
3b	0.73, 1.15	2	-5.53		
		irreversible oxidations			
	-1.95	1 reduction		-2.85	463
	-0.80	1			
3c	0.58,	3 oxidations	-5.38		
	0.83, 1.38				
	-0.01,	3 reductions			
	0.39, 0.54				
3d	-1.96, -	2 reductions		-2.84	488
	2.10				
	-0.81	1			
		reoxidation			
	0.51,	3 oxidations	-5.31		
	0.79, 1.38				
3a'	0.53, 0.30	2			
		rereductions			
	-1.01, -	2 reductions		-3.79	816
	2.22				
	-0.86, -	2			
	0.72	reoxidations			
3a'	0.72, 1.33	2 oxidation	-5.52		
	0.17, 0.42	2			
		rereductions			

^a Measured in 1.0 mM in CH_2Cl_2 , $[NBu_4][TfAB]$ vs. Fc^+/Fc

^b Calculated as $E(HOMO) = -4.80 - E_{pc}$ ⁴⁰

^c Calculated as $E(LUMO) = -4.80 - E_{pa}$

the analysis of the data obtained and comparison them with the known form the literature. From this point of view the description of optical data (UV/vis and emission spectroscopy), obtained for all compounds, may be regarded as a most complete.

Introduction of M_2 fragments into Th_n significantly change UV/vis absorption (bathochromic shift, increase of molar absorptivity) and improves the luminescence properties (increase of the Stokes shift and of the absolute quantum yield) compared to isolated fragments (see Table 1). This indicates that an effective σ - π -conjugation takes place in molecule. The same results are additionally confirmed by electrochemical data (Table 2). Thus, the first anodic oxidations of the compounds studied in this work

(approximately at 0.70 and 0.50 V vs. Fc/Fc^+) are likely to be the ones of the free Th_2 ($E_{\text{ox}} = 1.28$ V vs. Ag^+/AgCl) and Th_3 ($E_{\text{ox}} = 1.05$ V)⁴¹ groups. Furthermore, the potentials are diminished in comparison with Me_3MMMe_3 ($E_{1/2}$ 1.36/-0.59 V vs. Fc/Fc^+ for $\text{Me}_3\text{SiSiMe}_3$; $E_{1/2}$ 1.28/-0.46 V vs. Fc/Fc^+ for $\text{Me}_3\text{GeGeMe}_3$).⁴²

For the bithienyl derivatives based on silicon (Fig. S43a, ESI), the impact of the type of substitution of Th_2 and of the number of Si_2 chromophore on the absorption is straightforward. Increasing the number of Si_2 (Th_2Si_2 , **1a**, vs. $\text{Si}_2\text{Th}_2\text{Si}_2$, **2a**) and Th_2 (**1a** vs. **3a**) (Table 1) groups resulted in a bathochromic shift. The impact of Si_2 is more significant (compare $\text{Si}_2\text{Th}_2\text{Si}_2$, **2a**, and $\text{Th}_2\text{Si}_2\text{Th}_2$, **3a**). The intermediate value for the absorption of $[\text{Th}_2\text{Si}_2\text{Th}]_2$, **3a'**, may be explained by the non-planar (Th_2) or the non-*transoid* (ThSi_2Th) conformation,^{10d} which destroys the conjugation. Molecular absorptions of **2a**, **3a** and **3a'** (Table 1) is also more than twice greater indicating that in **3a'** the two chromophore fragments related to **2a/3a** are present.

For the terthienyl Ge compounds (Table 1; Fig. S43b, ESI), an evident red shift is observed when the number of Ge_2 groups (Th_3Ge_2 , **1b**, vs. $\text{Ge}_2\text{Th}_3\text{Ge}_2$, **2c**) is increased. Internal **3d**, $\text{Th}_3\text{Ge}_2\text{Th}_3$, is characterized by a significant hypsochromic shift, due to unordered Th_3 , which are only weakly conjugated. This indicates that a simple increase of the amount of Th in the chain conjugated would not be effective, especially for heavier Group 14 elements.

For the bithienyl germlylated compounds **2b**, $\text{Ge}_2\text{Th}_2\text{Ge}_2$, and **3b**, $\text{Th}_2\text{Ge}_2\text{Th}_2$ (Table 1; Fig. S44a, ESI), the absorption is similar to the one observed in the Si series: more germlylated **2b** shows a bathochromic shift and a higher molar absorptivity coefficient. In the terthienyl derivatives **3c**, $\text{Th}_3\text{Si}_2\text{Th}_3$, and **3d**, $\text{Th}_3\text{Ge}_2\text{Th}_3$ (Fig. S44b, ESI), it is evident that for germlylated derivative the apparent disruption of conjugation between the Th rings is observed, which makes the spectrum of **3d** is very similar to the one of **3b**, $\text{Th}_2\text{Ge}_2\text{Th}_2$.

In general, for silicon compounds the absorption bands are only modestly bathochromically shifted in comparison with their germlylated analogs; the terminal modification of thienyls groups has a greater effect than the modification of internal groups. The red shift is also due to the σ - π conjugation of M-M, M-C_{Me}⁴³ and the thienyl orbitals, this is why a stronger effect is observed for Si compounds than for Ge derivatives.

Conjugation between the Th_n and the M_2 fragments resulted in a significant Φ (Table 1) increase (from 3 to 76 % for bithienyl; from 8 to 19 % for terthienyl; from 5 to 76 % for Si_2 and from 2 to 19 % for Ge_2 ; compare with Th_n up to n 8, Φ up to 43 %⁴⁴). The biggest quantum yield is observed for $[\text{Th}_2\text{Si}_2\text{Th}]_2$, **3a'**, containing several conjugated Si_2 and Th_2 groups. At the same time increasing the number of Th rings (as in $\text{Th}_3\text{Si}_2\text{Th}_3$, **3c**) did not result to any increase. For the Si compounds, the observed quantum yield is higher than for the corresponding Ge derivatives ($\text{Si}_2\text{Th}_2\text{Si}_2$, **2a** vs. $\text{Ge}_2\text{Th}_2\text{Ge}_2$, **2b**). The small Stokes shift (66 nm) indicates a minimal geometry rearrangement of the excited state,⁴⁵ and therefore, the high emissivity and Stokes shift suggests a σ - σ^* transition.

The comparison the UV/vis absorption and luminescence

data for silicon compounds **1a**, **2a**, **3a**, **3a'** (316-332 nm) with the known for internal disilanes of the type $[(p\text{-XC}_6\text{H}_4)\text{SiMe}_2\text{SiMe}_2]_2\text{Ar}$ (X= OMe, NMe₂, OPh; CN, CO₂Et; Ar= benzothiadiazole, dimethylthieno[3,4-b]pyrazine, Th, Th_2 , 3,4-ethylenedioxythiophene)^{9d} (λ_{em} 391-504 nm as solid; λ_{em} 380-398 nm, Φ 0-40 % in CH_2Cl_2), starlike $\text{R}(\text{SiMe}_2[\text{Th}_2\text{Si}_2\text{Me}_2]_m\text{Th}_2)_n$ (R= MeSi, m= 0-2; n= 3; R= C₆H₃, m= 1-2; n= 3; R= C₆H₂, m= 1-2; n= 4) (λ_{abs} 321-337 nm, λ_{em} 380-398 nm, Φ 23-75 %),^{25a} $\text{C}_3\text{N}_3(\text{Th}_2\text{Si}_2)_3/\text{C}_3\text{N}_3(\text{Th}_2\text{Si}_2\text{Th}_2)_3$ (λ_{em} 451-452 nm, Φ 67-96 %),^{25e} or $\text{MeSi}[\text{SiMe}_2\text{TnSiMe}_2(t\text{-Bu})]_3$ ^{25b} (λ_{em} 374-529 nm, Φ 20-61 %, n= 2-6), monosilyl $[\text{C}_6\text{H}_{13}\text{Th}_2]_2\text{SiMe}_2$ ⁴⁶ (λ_{abs} 325 nm, λ_{em} 382 nm, Φ 9 %) or $[\text{Me}_3\text{SiTh}]_2$ (λ_{abs} 322 nm, λ_{em} 381 nm, Φ 6 %) and the polymeric $[\text{SiEt}_2\text{SiEt}_2\text{Th}]_n$ (λ_{abs} 343 nm, λ_{em} 383-397 nm, Φ 33 % in THF)⁴⁷ and $[\text{SiEt}_2\text{SiEt}_2\text{Th}]_n$ ^{26c} (λ_{em} 434 nm) compounds shows that the simple molecular compounds, obtained in this study, containing a minimal amounts of chromophores have almost identical or even improved characteristics. It means that under synthesis of more complex compounds, the features of the molecular structure (conformations, molecular contacts) play a significant role and may decrease the characteristics.

Theoretical (DFT) investigation

To clarify the electronic and luminescence spectra, DFT calculations were performed for model compounds.

The electronic distributions in internal (**3b**, $\text{Th}_2\text{Ge}_2\text{Me}_4\text{Th}_2$) (Figs. S49-S52, ESI) and in terminal germanium compounds (**2b**, $\text{Me}_5\text{Ge}_2\text{Th}_2\text{Ge}_2\text{Me}_5$) (Figs. S53-S56, ESI) are significantly different. For internal germanium compounds, the HOMO is spread over the entire molecule including the Th_2 and Ge_2 groups, but the LUMO, HOMO-1 and LUMO+1 are localized on the Th_2 , what is similar to what is observed for the related silicon derivatives.^{9b} In this case the excitation is transferred from the M_2 fragments to the Th_n and the absorption bands in the UV/vis region may be attributed to a $\text{S}_0 \rightarrow \text{S}_1$ transition (HOMO \rightarrow LUMO), indicating a intramolecular charge-transfer (ICT). On contrary, in terminal ($\text{Me}_5\text{Ge}_2\text{Th}_2\text{Ge}_2\text{Me}_5$) derivatives, the LUMO is located only on the Th_2 and the HOMO-1 and LUMO+1 are over all groups; the HOMO spreads over Th_2 and includes Ge_2 . Therefore, in the case of terminal Ge derivatives, other transitions types may be observed (HOMO \rightarrow LUMO+1, HOMO-1 \rightarrow LUMO), and the transitions may be regarded as an σ - σ^* excitation.

Calculations for terminal derivatives $\text{Me}_3\text{M}'\text{Me}_2\text{M}[\text{Th}]_n\text{MMe}_2\text{M}'\text{Me}_3$ in which the quantity of Th rings, nature of M/M' are different (Table S2, ESI), shows that with greater n, the UV/vis band is bathochromically shifted. Substitution of the M, conjugated with Th ring, by heavier atom (Si-Ge-Sn), resulted in a strong red shift for n= 1, but with further increase of n the values of theoretical UV/vis absorption bands are almost the same. This indicates the presence of a conjugation between the nearest Th and the M atom, and its weak dependence on the nature of M/M' nature.

For the internal derivatives $\text{Th}_2\text{MMe}_2\text{M}'\text{Me}_2\text{Th}_2$ (M, M'= Si, Ge, Sn; Table S3, ESI), the maximum absorption is observed for the Si-Ge derivative. On contrary to the above results for terminal derivatives, introduction of heavier atoms in general

Table 3. Luminescence emission data for $\text{Th}[\text{GeMe}_2]_n\text{Th}$ according to DFT calculations.

n	Absorption, λ_{abs} , nm	Fluorescence, λ_{em} , nm	$\Delta\lambda$, nm
1	224	256	32
2	258	324	66
3	261	369	108
4	263	441	178
5	261	516	255
6	261	543	283
7	258	546	288
8	271	349	78
9	266	348	82
10	266	363	97

results in a hypsochromic shift.

DFT calculations for **2a-b** and **3a-b** (Table S4, ESI) showed a good correlation between experiment (Table 1) and calculations. The substitution of the Si atom by a Ge atom has only small effect (low HOMO destabilization but bigger LUMO destabilization). Optical and electrochemical measurements of the resulting compounds and their DFT calculations indicated that the introduction of a Th unit enhances the conjugation along the molecule mainly by raising the HOMO energy level. The fluorescence data is in good correlation with the experiments performed on the solid state of our compounds, and the transitions correspond to the LUMO-HOMO.

Calculations for terminal derivatives $\text{Me}_3\text{GeGeMe}_2[\text{Th}]_n\text{GeMe}_2\text{GeMe}_3$ (Table S5, ESI) show that an increase of n results to a bathochromic shift of the UV absorption, each transition corresponds to the HOMO-LUMO transition. The gap, corresponding to this transition, decreases more significantly for small values of n (indicating a decrease of the π -conjugation with an increase of n ; compare with $[\text{SiEt}_2\text{SiEt}_2\text{Th}_m]_n$ where the σ - π -conjugation decreases with the increase the m ⁴⁸). The same trends are observed for luminescence (bathochromic shift, LUMO-HOMO transition, correlation with experimental data).

Furthermore, the effect of the number of Ge atoms (Table 3) indicates that the absorption gradually increases when the number of Ge atom is increasing from $n = 1$ to 4, but then the absorption decreases. It means that with the elongation of the Ge chain, the conformation of the molecule switches from a form favoring the σ -overlapping (Ge-Ge-Ge-Ge torsion is 180°)^{2, 14b} to another one, what results to appearance of several short-chain frameworks. On the other hand, the emission increases with the number of Ge atoms within a range from $n = 1$ to 8, what may be explained by the significant structural changes in the excited state in comparison with the fundamental state. Major changes are observed for small Ge chains while only minor effects are found for longer chains which might explain why polymers are only displaying minor effects. Thus, the simple elongation of Ge chain has the maximal effect, and neglected in polymers.

According to DFT calculations the physical properties of oligothieryl catenated Group 14 compounds highly depend on the nature of the Th_n groups (terminal or internal) and on the nature of M and on their conjugation. In addition, the overall conformation of the molecule allowing for the best

conjugation in solution/solid phase is also from prime importance. Furthermore, an effective stabilization of the excited states of oligothieryls by catenated Group 14 fragments is the more significant in the case of Th_2 than for Th_n .^{26d} For internal derivatives $\text{Th}_n\text{Ge}_2\text{Th}_n$ (Table S6, ESI) the larger red shifts and lower gap are observed than for terminal derivatives $\text{Me}_5\text{Ge}_2[\text{Th}]_n\text{Ge}_2\text{Me}_5$ (Table S5, ESI).

Conclusions

Several series of catenated oligosilanes and germanes were synthesized. These compounds have remarkable optical (UV/vis absorption, emission) and electrochemical properties in solution and in solid state. The fluorescence is characterized by an increased quantum yield, which in the case of molecular Si derivatives reaches up to 77 %. This effect is explained by the molecular structure and the efficient σ - π -conjugation between M_2 and the Th_n fragments. In general, for molecular oligothieryl catenated Group 14 derivatives improved optical characteristics (larger red shift, extinction coefficient, quantum yield) are observed compared to the free Th_n , whereas the solubility is increased also. The optical properties may be tuned by the modification of the structure (Si vs. Ge, number of Th rings, terminal or internal type of substitution). The optical properties of Si and Ge analogs are almost similar, but for the silicon derivatives the bands of absorption and fluorescence are slightly red shifted and the quantum yields are higher possibly due to a better orbital conjugation between the aryl and the Si_2 chromophores. The σ - π -conjugation is more significant for Th_2 than for Th_3 , this is especially evident for oligogermyl derivatives; furthermore, for longer terthienyl Group 14 derivatives the quantum yields are actually lower. In order to significantly improve the conjugation (π - and σ - π) it is necessary to insert bithiophenes, disubstituted by Group 14 fragments in terminal positions. Oligothieryl derivatives containing catenated Group 14 fragments are irreversibly oxidized without electropolymerization. Molecular compounds studied here may be regarded as models for polymers. The structure - property relationships established in this work are important for the future develop of new materials with specific physical properties. We are confident that these compounds will be used in a near future for various applications, for example, in the production of materials with conductive or emissive properties such as OLED.

Experimental Part

General Remarks. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. ^1H NMR (400.130 MHz), ^{13}C NMR (100.613 MHz) and ^{29}Si (79.495 MHz) spectra were recorded with a Bruker 400 or Agilent 400MR spectrometers at 298 K. Chemical shifts are given in ppm relative to internal Me_4Si (^1H , ^{13}C and ^{29}Si NMR spectra). Mass spectra (EI-MS, 70 eV) were recorded on a quadrupole mass spectrometer FINNIGAN MAT INCOS 50 with

direct insertion; all assignments were made with reference to the most abundant isotopes. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University using HeraeusVarioElementar instrument. UV/visible spectra were obtained using two ray spectrophotometer Evolution 300 «Thermo Scientific» with cuvette of 10.00 mm long. Fluorescence spectra at room temperature were recorded with Hitachi F-7000 luminescence spectrometer. The fluorescence quantum yields were measured using Rhodamine as reference; the error of the determination is 10% of the value obtained.

Materials. Solvents were dried using usual procedures. Tetrahydrofuran and diethyl ether were stored under solid KOH and then distilled over sodium/benzophenone. Toluene and *n*-hexane were refluxed and distilled over sodium. C₆D₆ was distilled over sodium under argon. CDCl₃ was distilled over CaH₂ under argon.

n-BuLi, ClSiMe₂SiMe₂Cl, ClSiMe₂SiMe₃ were used as supplied from commercial sources (Aldrich). 2,2'-Bithiophene (Th₂), 2,2':5',2''-terthiophene (Th₃), Ph₂GeMe₂, PhGeMe₂Br, PhGeMe₂H, PhGeMe₂GeMe₃, ClGeMe₂GeMe₃ were obtained by known methods using improved procedures (see ESI for further details). Silicagel 60 was used for column flash-chromatography.

Known compounds, Ph₂GeCl₂,^{21e} ClGeMe₂GeMe₂Cl,^{30, 49} were obtained by employing published procedures.

General procedure of monolithiation of 2,2'-bithiophene (Th₂) or 2,2':5',2''-terthiophene (Th₃). Synthesis of 5-Li(Th₂) or 5-Li(Th₃). At -78 °C solution of *n*-BuLi in *n*-hexane (2.5 M, 6.28 mmol, 1.10 eq.) was added dropwise to the solution of 2,2'-bithiophene or 2,2':5',2''-terthiophene (5.71 mmol, 1.00 eq.) in ether (50 mL). After 1 h the reaction mixture was slowly warmed to room temperature and stirred for 2 h. Then the mixture was cooled to -78 °C and used without further purification.

General procedure of dilithiation of 2,2'-bithiophene (Th₂) or 2,2':5',2''-terthiophene (Th₃). Synthesis of 5,5'-Li₂(Th₂) or 5,5'-Li₂(Th₃). The procedure is analogous to monolithiation using 2.1 eq. of *n*-BuLi.

General procedure for synthesis of 1a-b. At -78 °C solution of the corresponding silane or germane (6.28 mmol, 1.00 eq.) in ether (20 mL) was added dropwise to the solution of 5-Li(Th₂) or 5-Li(Th₃) (6.28 mmol, 1.00 eq.) in ether obtained as described above. Reaction mixture was slowly warmed to room temperature and stirred overnight. Saturated aqueous solution of NH₄Cl (40 mL) was added, water phase was extracted with ether (3x20 mL), combined organic phases were dried over MgSO₄ and all volatile materials were evaporated under reduced pressure. The residue obtained was purified by chromatography (SiO₂).

(2,2'-Bithiophene-5-yl)pentamethyldisilane, Th₂SiMe₂SiMe₃ (1a). Purified by column chromatography (SiO₂, petroleum ether, R_f 0.4). Compound **1a** (1.16 g, 62 %) was isolated as a yellowish oil, which solidifies in refrigerator (-30 °C) to yellow glass. ¹H NMR (δ, ppm, CDCl₃): 7.24, 7.08 (2d, each 1H, ³J_{H-H} = 3.5 Hz, thienyl protons), 7.21-7.17 (m, 2H, thienyl protons),

7.03-6.98 (m, 1H, thienyl proton), 0.38 (s, 6H, SiMe₂), 0.12 (s, 9H, SiMe₃). ¹³C NMR (δ, ppm, CDCl₃): 142.37, 138.80, 137.51 (3 thienyl quaternary carbons), 134.73, 127.75, 125.11, 124.21, 123.64 (thienyl CH carbons), -2.44 (SiMe₂), -2.82 (SiMe₃). ²⁹Si NMR (δ, ppm, CDCl₃): -19.22 (SiMe₃), -24.05 (SiMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 240 (4.6×10³), 316 (1.6×10⁴). MS (EI) *m/z* 297 ([M]⁺, 21), 296 ([M - 1]⁺, 94), 281 ([M - Me]⁺, 57), 223 ([M - SiMe₃]⁺, 100), 208 ([M - SiMe₃ - Me]⁺, 10), 165 ([Th₂ - H]⁺, 3), 133 ([Th₂ - S - H]⁺, 18). Anal. Calcd. for C₁₃H₂₀S₂Si₂ (296.5989): C, 52.64; H, 6.80. Found: C, 52.05; H, 6.98.

(2,2':5',2''-terthiophene-5-yl)pentamethyldigermene, Th₃GeMe₂GeMe₂ (1b). Purified by column chromatography (SiO₂, petroleum ether, R_f 0.4). Compound **1b** (1.65 g, 56 %) was isolated as a colorless oil which slowly solidified into colorless powder, m.p. 83-84 °C. ¹H NMR (δ, ppm, CDCl₃): 7.23-7.19, 7.09-7.05, 7.03-6.98 (3m, each 2H, thienyl protons), 7.18-7.15 (m, 1H, thienyl proton), 0.54 (s, 6H, GeMe₂), 0.31 (s, 9H, GeMe₃). ¹³C NMR (δ, ppm, CDCl₃): 141.47, 140.42, 136.10, 124.79, 123.53 (5 thienyl quaternary carbons), 133.61, 127.87, 124.64, 124.47, 124.32, 124.04, 123.69 (thienyl CH carbons), -2.26 (GeMe₂), -2.32 (GeMe₃). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 246 (8.7×10³), 366 (2.1×10⁴). MS (EI) *m/z* 468 ([M]⁺, 24), 453 ([M - Me]⁺, 3), 438 ([M - GeMe₂]⁺, 22), 350 ([Th₃GeMe₂]⁺, 6), 248 ([Th₃]⁺, 21), 215 ([Th₃ - S - H]⁺, 10), 202 ([Th₃ - CHS]⁺, 6), 171 ([Th₃ - CHS - S]⁺, 4), 118 ([Me₃Ge]⁺, 100). Anal. Calcd. for C₁₇H₂₂Ge₂S₃ (467.8316): C, 43.64; H, 4.74. Found: C, 42.87; H, 4.86.

General procedure for synthesis of 2a-c. The procedure is analogous to the one described above using 5,5'-Li₂(Th₂) or 5,5'-Li₂(Th₃) (6.28 mmol, 1.00 eq.) and corresponding silane or germane (12.56 mmol, 2.00 eq.).

(2,2'-Bithiophene-5,5'-diyl)bis(pentamethyldisilane),

Me₃SiSiMe₂Th₂SiMe₂SiMe₃ (2a). Purified by chromatography (SiO₂, petroleum ether, R_f 0.6) and then by recrystallization from minimal quantity of MeOH. Compound **2a** (1.18 g, 44 %) was isolated as a yellowish plates, m.p. 72-73 °C. ¹H NMR (δ, ppm, CDCl₃): 7.24, 7.07 (2d, each 2H, ³J_{H-H} = 3.5 Hz, thienyl protons), 0.38 (s, 12H, 2SiMe₂), 0.12 (s, 18H, 2SiMe₃). ¹³C NMR (δ, ppm, CDCl₃): 142.46, 138.62 (2 thienyl quaternary carbons), 134.76, 125.01 (thienyl CH carbons), -2.43 (SiMe₂), -2.83 (SiMe₃). ²⁹Si NMR (δ, ppm, CDCl₃): -19.31 (SiMe₃), -24.14 (SiMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 246 (3.9×10³), 332 (2.1×10⁴). MS (EI) *m/z* 427 ([M]⁺, 29), 412 ([M - Me]⁺, 9), 354 ([M - SiMe₃]⁺, 100), 336 ([M - SiMe₂ - S]⁺, 50), 321 ([M - SiMe₃ - S]⁺, 29), 296 ([M - Si₂Me₅]⁺, 6), 281 ([M - Si₂Me₅ - Me]⁺, 3), 266 ([M - 2SiMe₃ - Me]⁺, 39), 248 ([M - 2SiMe₃ - S]⁺, 5), 233 ([M - 2SiMe₃ - S - Me]⁺, 7), 165 ([Th₂ - H]⁺, 11), 131 ([Si₂Me₅]⁺, 8), 115 ([Si₂Me₄ - H]⁺, 7), 73 ([SiMe₃]⁺, 70). Anal. Calcd. for C₁₈H₃₄S₂Si₄ (426.9346): S, 15.02; C, 50.64; H, 8.03. Found: S, 14.99; C, 50.40; H, 8.01.

(2,2'-Bithiophene-5,5'-diyl)bis(pentamethyldigermene),

Me₃GeGeMe₂Th₂GeMe₂GeMe₃ (2b). Purified by chromatography (SiO₂, petroleum ether, R_f 0.5) and then by recrystallization from minimal quantity of MeOH. Compound **2b** (2.01 g, 53 %) was isolated as a colorless oil, which solidifies in a refrigerator at -30 °C to white needles, m.p. 70-71 °C. ¹H NMR (δ, ppm, CDCl₃): 7.21, 6.99 (2d, each 2H, ³J_{H-H} = 3.3 Hz,

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thienyl protons), 0.53 (s, 12H, 2GeMe₂), 0.30 (s, 18H, 2GeMe₃). ¹³C NMR (δ, ppm, CDCl₃): 141.84, 139.85 (2 thienyl quaternary carbons), 133.51, 124.57 (thienyl CH carbons), -2.28 (GeMe₂), -2.34 (GeMe₃). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 235 (1.6×10⁴), 325 (3.9×10⁴). MS (EI) *m/z* 605 ([M]⁺, 3), 590 ([M - Me]⁺, 2), 545 ([M - 4Me]⁺, 16), 502 ([M - GeMe₂]⁺, 1), 487 ([M - GeMe₃]⁺, 14), 385 ([M - Ge₂Me₅]⁺, 37), 370 ([M - Ge₂Me₅ - Me]⁺, 6), 355 ([M - 2GeMe₃ - Me]⁺, 39), 340 ([Th₂Ge₂Me₂]⁺, 8), 268 ([Th₂GeMe₂]⁺, 12), 220 ([Ge₂Me₅]⁺, 3), 205 ([Ge₂Me₄]⁺, 9), 165 ([Th₂ - H]⁺, 1), 120 ([Th₂ - CS]⁺, 43), 118 ([GeMe₃]⁺, 100). Anal. Calcd. for C₁₈H₃₄Ge₄S₂ (605.1526): C, 35.73; H, 5.66. Found: C, 35.27; H, 5.62.

(2,2':5',2''-terthiophene-5,5''-diyl)bis(pentamethyldigermene), Me₅Ge₂Th₃Ge₂Me₅ (2c).

Purified by chromatography (SiO₂, petroleum ether, R_f 0.7). Compound **2c** (2.64 g, 62 %) was isolated as a colorless powder, m.p. 108–109 °C. ¹H NMR (δ, ppm, CDCl₃): 7.22, 7.01 (2d, each 2H, ³J_{H-H} = 3.4 Hz, thienyl protons), 7.05 (s, 2H, thienyl protons), 0.54 (s, 12H, 2GeMe₂), 0.31 (s, 18H, 2GeMe₃). ¹³C NMR (δ, ppm, CDCl₃): 141.47, 140.41, 136.10 (3 thienyl quaternary carbons), 133.60, 124.63, 124.03 (3 thienyl CH carbons), -2.26 (GeMe₂), -2.32 (GeMe₃). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 240 (1.4×10⁴), 372 (3.7×10⁴). MS (EI) *m/z* 687 ([M]⁺, 100), 672 ([M - Me]⁺, 5), 626 ([M - 4Me]⁺, 23), 585 ([M - GeMe₂]⁺, 14), 570 ([M - GeMe₃]⁺, 25), 524 ([M - GeMe₃ - 3Me]⁺, 17), 509 ([M - GeMe₃ - 4Me]⁺, 17), 482 ([M - Ge₂Me₄]⁺, 32), 467 ([M - Ge₂Me₅]⁺, 23), 437 ([M - Ge₂Me₅ - 2Me]⁺, 36), 423 ([M - Ge₂Me₅ - CS]⁺, 2), 349 ([M - Ge₂Me₅ - GeMe₃]⁺, 6), 333 ([M - Ge₂Me₅ - GeMe₃ - Me]⁺, 3), 220 ([Ge₂Me₅]⁺, 2), 119 ([Me₃Ge - H]⁺, 19). Anal. Calcd. for C₂₂H₃₆Ge₄S₃ (687.2762): C, 38.45; H, 5.28. Found: C, 37.96; H, 5.14.

General procedure for synthesis of 3a-d. The procedure is analogous to the one described above using Li(Th₂) or 5-Li(Th₃) (12.56 mmol, 1.00 eq.) and corresponding silane or germane (6.28 mmol, 0.50 eq.).

1,2-Bis(2,2'-bithiophene-5-yl)-1,1,2,2-tetramethyldigermene, Th₂SiMe₂SiMe₂Th₂ (3a).

Purified by column flash-chromatography (SiO₂, petroleum ether:toluene= 40:1, R_f 0.3). Compound **3a** (1.18 g, 42 %) was isolated as a yellowish crystals, m.p. 108–109 °C. ¹H NMR (δ, ppm, CDCl₃): 7.27–7.24, 7.09–7.06, 7.02–6.99 (3m, each 2H, thienyl protons), 7.21–7.18 (m, 4H, thienyl protons), 0.45 (s, 12H, 2SiMe₂). ¹³C NMR (δ, ppm, CDCl₃): 142.78, 137.37, 137.32 (3 thienyl quaternary carbons), 135.31, 127.78, 125.20, 124.35, 123.79 (5 thienyl CH carbons), -2.83 (SiMe₂). ²⁹Si NMR (δ, ppm, CDCl₃): -24.56 (SiMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 248 (7.6×10³), 321 (2.0×10⁴). MS (EI) *m/z* 447 ([M]⁺, 26), 432 ([M - Me]⁺, 65), 357 ([M - 2HCS]⁺, 100), 341 ([M - 2HCS - Me]⁺, 42), 281 ([Th₂Si₂Me₄]⁺, 3), 223 ([Th₂SiMe₂]⁺, 98), 207 ([Th₂SiMe - H]⁺, 23), 193 ([Th₂Si]⁺, 10), 148 ([Th₂Si - CHS]⁺, 11), 133 ([Th₂ - S - H]⁺, 43), 115 ([Si₂Me₄ - H]⁺, 43). Anal. Calcd. for C₂₀H₂₂S₄Si₂ (446.8197): S, 28.71; C, 53.76; H, 4.96. Found: S, 29.24; C, 53.63; H, 4.64.

5,5'-Bis[(1,1,2,2-tetramethyldisilyl-2-(2,2'-bithiophene-5-yl))-2,2'-bithiophene, [Th₂SiMe₂SiMe₂Th]₂ (3a'). It was isolated as a second fraction at synthesis of **3a** after chromatography (SiO₂, petroleum ether:toluene= 20:1, R_f 0.5). Compound **3a'**

(0.37 g, 16 %) was isolated as green-yellowish plates after recrystallization from isopropanol, m.p. 123–124 °C. ¹H NMR (δ, ppm, CDCl₃): 7.25–7.23, 7.21–7.17, 7.07–7.04 (3m, each 4H, thienyl protons), 7.02–6.98 (m, 2H, thienyl protons), 0.43 (s, 24H, 4SiMe₂). ¹³C NMR (δ, ppm, CDCl₃): 142.76, 142.73, 137.37, 137.32 (thienyl quaternary carbons), 135.36, 135.31, 127.79, 125.25, 125.20, 124.34, 123.78 (thienyl CH carbons), -2.84 (SiMe₂). Two thienyl quaternary signals are overlapped. ²⁹Si NMR (δ, ppm, CDCl₃): -24.34 (br, SiMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 233 (2.2×10⁴), 327 (5.7×10⁴). MS (EI) *m/z* 727 ([M]⁺, 41), 654 ([M - 5Me]⁺, 2), 637 ([M - 2CHS/6Me]⁺, 53), 546 ([M - Th₂ - Me]⁺, 7), 503 ([M - Th₂SiMe₂]⁺, 44), 488 ([M - Th₂SiMe₂ - Me]⁺, 7), 445 ([Th₂Si₂Me₄Th₂ - H]⁺, 6), 432 ([Th₂Si₂Me₄Th₂ - Me]⁺, 1), 357 ([Th₂Si₂Me₄Th₂ - 2HCS]⁺, 100), 341 ([Th₂Si₂Me₄Th₂ - 2HCS - Me]⁺, 1), 281 ([Th₂Si₂Me₄]⁺, 6), 265 ([Th₂SiMe₂SiMe - H]⁺, 5), 223 ([Th₂SiMe₂]⁺, 100), 207 ([Th₂SiMe - H]⁺, 11), 165 ([Th₂ - H]⁺, 4), 133 ([Th₂ - S - H]⁺, 14), 115 ([Si₂Me₄ - H]⁺, 11). Anal. Calcd. for C₃₂H₃₈S₆Si₄ (727.3761): C, 52.84; H, 5.27. Found: C, 52.27; H, 5.44.

1,2-Bis(2,2'-bithiophene-5-yl)-1,1,2,2-tetramethyldigermene, Th₂GeMe₂GeMe₂Th₂ (3b).

Purified by column flash-chromatography (SiO₂, petroleum ether, R_f 0.3) and then treated by methanol. Compound **3b** (2.19 g, 65 %) was isolated as yellow crystals after recrystallization from *n*-hexane, m.p. 97–98 °C. ¹H NMR (δ, ppm, CDCl₃): 7.23 (d, 2H, ³J_{H-H} = 3.4 Hz, thienyl protons), 7.20 (dd, 2H, ³J_{H-H} = 5.1 Hz, ³J_{H-H} = 1.3 Hz, thienyl protons), 7.19 (dd, 2H, ³J_{H-H} = 3.4 Hz, ³J_{H-H} = 1.0 Hz, thienyl protons), 7.03–6.98 (m, 4H, thienyl protons), 0.62 (s, 12H, 2GeMe₂). ¹³C NMR (δ, ppm, CDCl₃): 142.03, 138.64, 137.45 (3 thienyl quaternary carbons), 134.01, 127.75, 124.96, 124.19, 123.63 (5 thienyl CH carbons), -2.07 (GeMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 235 (8.4×10³), 319 (1.8×10⁴). MS (EI) *m/z* 536 ([M]⁺, 48), 521 ([M - Me]⁺, 8), 472 ([M - 2S]⁺, 2), 446 ([M - 2HCS]⁺, 2), 268 ([Th₂GeMe₂]⁺, 100), 253 ([Th₂GeMe]⁺, 1), 238 ([Th₂Ge]⁺, 25), 165 ([Th₂ - H]⁺, 2), 133 ([Th₂ - S - H]⁺, 24). Anal. Calcd. for C₂₀H₂₂Ge₂S₄ (535.9287): C, 44.82; H, 4.14. Found: C, 45.12; H, 4.35.

1,2-Bis(2,2':5',2''-terthiophene-5-yl)-1,1,2,2-tetramethyldigermene, Th₃SiMe₂SiMe₂Th₃ (3c).

Purified by column flash-chromatography (SiO₂, petroleum ether, then petroleum ether:toluene= 7:1, R_f 0.4) and then treated by methanol. Compound **3c** (1.50 g, 39 %) was isolated as yellowish powder, m.p. 135–136 °C. ¹H NMR (δ, ppm, CDCl₃): 7.23–7.20 (m, 4H, thienyl protons), 7.18–7.15, 7.03–6.99 (2m, each 2H, thienyl protons), 7.08–7.05 (m, 6H, thienyl protons), 0.44 (s, 12H, 2SiMe₂). ¹³C NMR (δ, ppm, CDCl₃): 142.50, 137.57, 137.20, 136.22, 136.17 (5 thienyl quaternary carbons), 136.39, 127.88, 125.11, 124.41, 124.35, 123.63 (6 thienyl CH carbons), -2.86 (SiMe₂). Two thienyl CH carbon signals are overlapped. ²⁹Si NMR (δ, ppm, CDCl₃): -24.44 (SiMe₂). UV/vis (CH₂Cl₂) λ_{max} nm (ε, M⁻¹ cm⁻¹): 250 (2.0×10⁴), 366 (5.4×10⁴). MS (EI) *m/z* 611 ([M]⁺, 26), 596 ([M - Me]⁺, 4), 521 ([M - 2HCS]⁺, 45), 364 ([Th₃Si₂Me₄]⁺, 3), 306 ([Th₃SiMe₂]⁺, 100), 215 ([Th₃ - S - H]⁺, 44), 171 ([Th₃ - CHS - S]⁺, 14), 115 ([Me₄Si₂ - H]⁺, 17). Anal. Calcd. for C₂₈H₂₆S₆Si₂ (611.0670): C, 55.03; H, 4.29. Found: C, 55.26; H, 3.96.

1,2-Bis(2,2':5',2''-terthiophene-5-yl)-1,1,2,2-tetramethyldigermene, $\text{Th}_3\text{GeMe}_2\text{GeMe}_2\text{Th}_3$ (3d**).** Purified by column flash-chromatography (SiO_2 , petroleum ether, then petroleum ether:toluene = 7:1; R_f 0.2) and then recrystallized from *n*-hexane. Compound **3d** (1.85 g, 42 %) was isolated as yellow crystals, m.p. 129–130 °C. ^1H NMR (δ , ppm, CDCl_3): 7.23 (d, 2H, $^3J_{\text{H-H}} = 3.5$ Hz, thienyl protons), 7.21 (dd, 2H, $^3J_{\text{H-H}} = 5.2$ Hz, $^3J_{\text{H-H}} = 1.2$ Hz, thienyl protons), 7.16 (dd, 2H, $^3J_{\text{H-H}} = 3.7$ Hz, $^3J_{\text{H-H}} = 1.2$ Hz, thienyl protons), 7.09–7.05, 7.03–6.99 (2m, each 4H, thienyl protons), 0.63 (s, 12H, 2GeMe₂). ^{13}C NMR (δ , ppm, CDCl_3): 141.74, 138.90, 137.23, 136.25, 136.04 (5 thienyl quaternary carbons), 134.11, 127.85, 124.85, 124.37, 124.33, 124.18, 123.59 (7 thienyl CH carbons), -2.09 (GeMe₂). UV/vis (CH_2Cl_2) λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 246 (1.8×10^4), 318 (4.7×10^4). MS (EI) m/z 700 ($[\text{M}]^+$, 18), 655 ($[\text{M} - \text{HCS}]^+$, 2), 598 ($[\text{M} - \text{GeMe}_2 + \text{H}]^+$, 2), 350 ($[\text{Th}_3\text{GeMe}_2]^+$, 100), 321 ($[\text{Th}_3\text{Ge} + \text{H}]^+$, 42), 248 ($[\text{Th}_3]^+$, 2), 215 ($[\text{Th}_3 - \text{S} - \text{H}]^+$, 2), 202 ($[\text{Th}_3 - \text{CHS}]^+$, 9), 171 ($[\text{Th}_3 - \text{CHS} - \text{S}]^+$, 10). Anal. Calcd. for $\text{C}_{28}\text{H}_{26}\text{Ge}_2\text{S}_6$ (700.1760): C, 48.03; H, 3.74. Found: C, 48.31; H, 3.59.

Conflicts of interest

There are no conflicts to declare.

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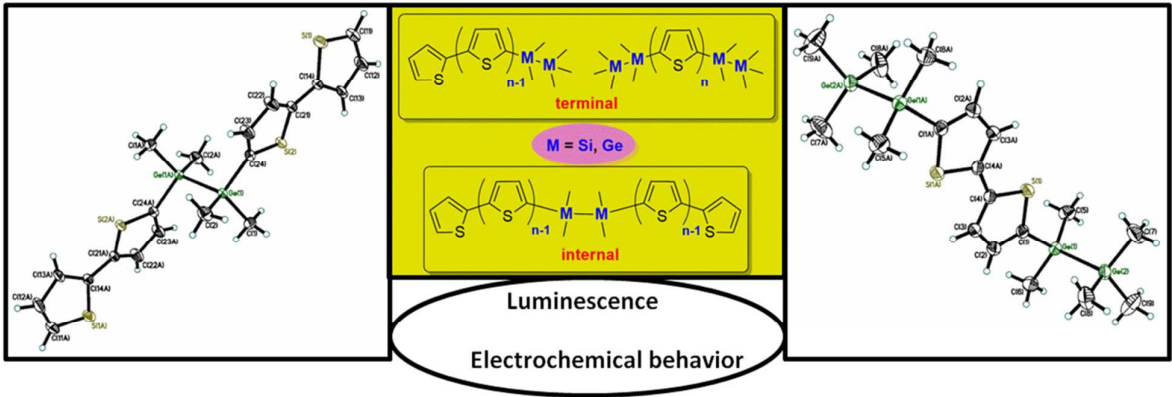
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A series of catenated terminal and internal Group 14 oligothiophenyl derivatives was obtained; their structural, electrochemical, optical properties were investigated.